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THE DIELECTRIC PROPERTIES OF THE CONSTITUENTS OF LAC

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ABSTRACT. The dielectric properties of the chief constituents of lac, *viz.*, pure lac, soft lac and lac-wax, have been measured separately over a wide range of temperature and frequency. The dielectric constant as well as pure a.c. loss-factor for all these components show typical dipolar characteristics regarding temperature and frequency variation. A distributed range of relaxation times for the first two components has been established and these distribution coefficients calculated. The calculation of the average diameter of soft lac resin rotator shows that as in whole lac, the hydroxyl group is the main polar group responsible for dieletric loss. Measurement of viscosity of soft lac over a range of temperature shows that the logarithmic law, meant for liquids, is strictly followed by it regarding the variation of temperature. The values of activation energy calculated from viscosity data as well as d.c. conductance data of soft lac agree quite well. They also agree with the activation energy obtained from a.c. data. No transition point could be observed for soft lac but hard lac exhibits such a point near about 50°C. The anomalous dispersion of lac-wax has been observed near its softening point although the extent of dielectric constant variation is small.

INTRODUCTION

It has been observed recently (Bhattacharya, 1944) that lac as such behaves as a typical polar resin. It shows anomalous dispersion at ordinary temperatures and the maximum dielectric loss for any frequency takes place at a definite temperature. The loss curve is a typical absorption curve which shifts towards high temperature side with the increase of frequency. But having a comparatively large molecule it has a distributed rage of relaxation times due to which it has a wide dispersion range as well as a diminished value of maximum dielectric loss. The application of Stoke's law in order to calculate the radius of the 'lac molecule' has revealed the interesting fact that only the hydroxyl group of the molecule is responsible for the loss and probably the general rotation of the whole molecule does not take place. But lac, as we know now, is a mixture of a few constituents. It is of interest, therefore, to study the dielectric properties of these constituents in order to understand the dielectric behaviour of lac in a better way.

There are three constituents of lac—(*i*) pure lac resin, α-lac or simply hard lac, (*ii*) soft lac and (*iii*) lac-wax. Pure lac is insoluble in diethyl ether but soluble in alcohol, while soft lac is soluble in moist ether. Pure lac is the main fraction of lac comprising about 70% of the whole, soft lac comprises 25-30%, whilst lac-wax is only about 4% of the total. Lac-wax is again a mixture of two main fractions according to its solubility in alcohol. The alcohol-soluble fraction is the main constituent comprising more than 6/7 of the whole and the alcohol insoluble but benzene soluble part comprises only 1/7 of the total wax. These two main fractions are again mixtures of several components.

Pure lac softens at a higher temperature than whole lac, does not melt to a thin fluid and readily hardens at high temperatures. Soft lac, on the other hand, is a cooled glass-like substance at low temperatures, becoming a thin fluid at higher temperatures and is not easily hardened by heat.

From the results of the study of dielectric properties of individual components of lac it can easily be seen if of the two main components one is very different from the other regarding dielectric loss and if so whether the exclusion of one or the other constituent from lac results in a better product in this respect.

The electrical industry, in general, prefers to use de-waxed lac instead of whole lac. This has, in certain quarters, given rise to the notion that the dielectric properties of lac-wax are

undesirable (Rangaswami & Sen, 1942) although there seems to be no such record which can justify this view. An elaborate study of the dielectric properties of the constituents of lac may naturally throw light on many such practices which are being observed in many industries even today.

THEORETICAL

The complex dielectric constant ϵ of a substance is usually expressed as

$$\epsilon = \epsilon' - i\epsilon''$$

where ϵ' = the real or the ordinary dielectric constant,

and ϵ'' = the imaginary part of it or the dielectric loss factor.

The dielectric loss factor is related to the ordinary dielectric constant through a factor which is usually called the power factor and is generally expressed as $\cos\phi$ where ϕ is the phase angle, *i.e.*, the angle between the applied voltage and the current vectors. This relation is $\epsilon'' = \epsilon' \cos\phi$. The complementary phase angle is called the loss angle and is generally expressed by δ. Hence

$$\epsilon'' = \epsilon' \cos\phi = \epsilon' \sin\delta = \epsilon' \tan\delta, \text{ since } \delta \text{ is usually very small.} \quad \ldots (1)$$

From the known values of dielectric constant power factor, $\tan\delta$ (both of which may be determined over a Schering bridge or a capacity bridge), the dielectric loss may be computed.

Now for a condenser having dielectric loss, the current in phase with the applied voltage may be expressed as

$$I_r = I \sin\delta = I \tan\delta, \text{ since } \delta \text{ is small.} \quad \ldots (2)$$

And the expression for current through a condenser C when an alternating voltage V is impressed at its terminals is

$$I = \omega CV \quad \ldots (3)$$

Therefore substituting in (2) for I, we have

$$I_r = \omega CV \tan\delta \quad \ldots (4)$$

But $\tan\delta = \epsilon''/\epsilon'$ from (1) and substituting this value of $\tan\delta$ in (4) we can further write

$$I_r = \omega CV\frac{\epsilon''}{\epsilon'} = 2\pi f CV\frac{\epsilon''}{\epsilon'} \quad \ldots (5)$$

Again for a parallel plate condenser the capacity C of a condenser is given by

$$C = \frac{A\epsilon'}{4\pi d\ 9 \times 10^{11}} \text{ farads} \quad \ldots (6)$$

where A, d and ϵ' are the effective area, the thickness and the dielectric constant respectively of the insulating material of the condenser. Substituting this value of C in (5), we have

$$I_r = 2\pi f.\frac{AV\epsilon'}{4\pi d9 \times 10^{11}} \cdot \frac{\epsilon''}{\epsilon'} = \frac{fAV\epsilon''}{d18 \times 10^{11}} \quad \ldots (7)$$

If however K_t is the total specific conductivity of the dielectric of the condenser comprising both the d.c. conductivity K_0 and the a.c. conductivity K, this may be written as

$$K_t = K_0 + K \quad \ldots (8)$$

And the current I_r may therefore be represented as

$$I_r = \frac{AVK_t}{d} \quad \ldots (9)$$

Hence from (7) and (9), we obtain the relation

$$\epsilon'' f = 18 \times 10^{11} K_t \qquad \ldots \quad (10)$$

The total specific conductivity in this expression yields the value of total dielectric loss on computation. Pure a.c. dielectric loss may, however, be ascertained by taking the a.c. conductivity value K instead of K_t in the above expression. Hence the expression for pure a.c. dielectric loss is

$$\epsilon'' = \frac{18 \times 10^{11} \times K}{f} \qquad \ldots \quad (11)$$

EXPERIMENTAL

Apparatus.—For the lower frequencies a Schering bridge was used for the determination of dielectric constant and power factor and for the higher frequencies a radio-frequency bridge was employed. The details of the bridges, detectors and the sources of current supply used in this investigation have been previously reported (Bhattacharya, 1944).

Electrodes.—The vertical type parallel plate gold condenser, described previously, was employed for soft lac resin and shellac wax, but for hard lac resin (α-lac) tin foil electrodes backed by hollow metal electrodes for the circulation of oil from a thermostat for controlling temperature could only be used. These have also been described earlier.

Materials.—Soft lac resin was obtained by Soxhlet extraction with diethyl ether from a sample of Kusmi shellac. This resin was then dissolved in ethyl acetate and boiled with decolourising charcoal to remove any colouring matter. After this treatment the soft resin was again boiled with petroleum ether under a reflux and the resin was vigorously stirred from time to time with a glass rod. After a few renewal of the petroleum ether, the soft resin was almost free from any wax, and this soft lac was heated at about 100°C in a vacuum-oven till it was free from any adherent solvent.

Hard lac resin was prepared from a sample of Kusmi lac by Soxhlet extraction with ether. Lac was ground to a fine powder, mixed with quartz sand and repeatedly extracted first with diethyl ether and then with petroleum ether in Soxhlet apparatus for the removal of soft lac resin and shellac wax. Finally the resin was dissolved in alcohol, filtered free from sand, precipitated again from a large volume of distilled water and then drawn into fibre on softening from the boiling water. These fibres were dried in air, powdered in a mortar and then finally dried in a vacuum-oven at 40°C.

Shellac wax was obtained by purifying Angelo Bros.' commercial shellac wax. The commercial wax was dissolved in benzene, boiled with decolourising charcoal under a reflux for 3 hours and then filtered. The wax recovered from the solution, after freeing it from the adherent solvent, was used for the experiments.

Method of procedure.—Soft lac resin and shellac wax could be melted at a higher temperature without any difficulty and so the vertical parallel plate condenser was used for their measurements. Detailed procedure regarding precautions to be taken to avoid adherent air bubbles, etc., has been given in the earlier paper. Shellac wax has a large contraction on solidification and so the molten wax was slowly allowed to solidify from the bottom in order that void formation may be avoided.

A few 4″ discs were moulded out of hard lac resin using a very small quantity of stearic acid as mould lubricant. Higher pressure was necessary to mould hard lac than is generally

necessary for whole lac. The technique was the same as described previously (Bhattacharya, 1942). After about 80°C the discs began to soften and further readings could only be obtained with difficulty up to 90°C. But unlike whole lac hard lac could not be melted to such a degree of fluidity that the parallel plate condenser could be dipped in that molten mass. It was, therefore, not possible to obtain for hard lac readings at temperatures higher than 90°C.

CALCULATIONS

The formulæ used for the calculation of air capacitance of the test condenser, the correction for edge-capacitance of the condenser, etc., have been given in the previous paper.

RESULTS

(a) *Soft lac resin*

TABLE I

Dielectric constant—temperature data at different frequencies

Frequency in Kc/s	Dielectric constant ϵ' at the temperature of (°C)									
	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
500	3·35	3·52	3·74	3·99	4·24	4·60	4·99	5·33	5·55	5·71
100	3·46	3·68	3·94	4 24	4·56	5·10	5·56	5·86	6·00	6·06
50	3·50	3·75	4 06	4·38	4·76	5·36	5 82	6·08	6·13	6·14
25	3·56	3·80	4·14	4·50	4·92	5·60	6·06	6·28	6·28	6·22
10	3·60	3·90	4·26	4·68	5·20	5·96	6·28	6·38	6·36	6·30
5	3·66	3·95	4·36	4·82	5·44	6·12	6·53	6·44	6·40	6·34
3	3·70	4·01	4·46	4·99	5·61	6·27	6·48	6·51	6 46	6·40
2	3·76	4·08	4·55	5·11	5·88	6·43	6·60	6·62	6·57	6·50
1	3·84	4·19	4·70	5·34	6·11	6·70	6·72	6·66	6·60	6·53
0·5	3·95	4·33	4·92	5·73	6·59	6·90	6·88	6·79	6·66	6·54
0·05	4·20	4·87	5·80	6·55	6·90	7·02	7·00	6·87	—	—

TABLE II

Measured power factor data at different temperatures and frequencies

Frequency in Kc/s	Power factor (uncorrected for D.C. conductivity) at the temperature of (°C)									
	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
500	.0304	.0405	0499	.0564	.0666	.0802	.0864	.0920	.0785	.0674
100	.0303	.0387	.0483	.0603	.0716	.0821	.0873	0736	.0565	.0428
50	.0308	0389	.0485	.0633	.0752	.0842	.0829	.0668	.0509	0337
25	.0287	.0389	.0516	.0654	.0796	.0894	.0708	.0530	.0369	.0333
10	.0260	.0391	.0535	.0691	.0833	.0805	.0592	0421	.0360	.0396
5	.0230	0384	.0548	.0719	.0862	.0673	0499	0354	.0352	.0558
3	.0227	.0391	.0563	.0752	.0830	.0589	.0427	.0344	.0426	.0814
2	.0236	.0384	.0583	.0806	.0757	.0544	.0394	.0374	.0532	.1420
1	.0181	.0361	.0601	.0870	.0662	.0427	.0316	.0502	.0850	—
0.5	.0176	.0370	.0672	.0823	.0581	.0373	.0431	.0742	—	—
0.05	.0042	.0601	.0802	.0568	.0500	—	—	—	—	—

TABLE III

Total A.C. conductivity data at different temperatures and frequencies

Frequency in Kc/s	Calculated ($K_t \times 10^8$) values from measured power factor at (°C)									
	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
500	2.831	3.959	5.186	6.250	7.841	10.25	12.39	13.62	12.12	10.69
100	0.582	0.791	1.056	1.421	1.813	2.326	2.697	2.396	1.884	1.442
50	0.299	0.405	0.546	0.771	0.995	1.254	1.307	1.127	0.867	0.575
25	0.142	0.206	0.296	0.409	0.544	0.695	0.596	0.515	0.323	0.288
10	0.052	0.085	0.127	0.180	0.241	0.267	0.206	0.149	0.127	0.139
5	0.023	0.042	0.066	0.096	0.130	0.114	0.088	0.063	0.062	0.098
3	0.014	0.026	0.042	0.063	0.078	0.062	0.046	0.037	0.046	0.087
2	0.009	0.017	0.029	0.046	0.049	0.039	0.029	0.028	0.039	0.102
1	0.004	0.008	0.016	0.026	0.022	0.016	0.012	0.019	0.031	0.067
0.5	0.002	0.004	0.009	0.013	0.011	0.007	0.008	0.014	—	—
0.05	—	0.001	0.002	0.001	—	—	—	—	—	—

TABLE IV

Resistivity or conductivity—temperature data

Temperature		$1/T \times 10^3$	Resistivity $\rho_0 \times 10^{-12}$	D.C. Conductivity $K_0 \times 10^{12}$	$\log \rho_0$
t°C	T°K				
20°	293	3.413	121	0.008	14.08
30°	303	3.300	25.0	0.040	13.40
40°	313	3.195	3.60	0.278	12.56
50°	323	3.096	0.57	1.750	11.76
60°	333	3.003	0.08	12.50	10.90
70°	343	2.915	0.022	45.40	10.34
80°	353	2.833	0.005	200.0	9.70
90°	363	2.755	0.002	500.0	9.30

TABLE V

Dielectric loss—temperature data at different frequencies

Frequency in Kc/s	Dielectric loss ϵ'' (Corrected for D.C. conductivity) at the temperature of (°C)								
	10°	20°	30°	40°	50°	60°	70°	80°	90°
500	.1019	.1425	.1866	.2250	.2823	3692	.4300	.4901	.4320
100	.1047	.1423	.1901	.2558	.3265	.4180	.4845	.4260	.3302
50	.1076	.1457	.1966	.2774	.3581	.4500	4800	.4001	.2901
25	.1023	.1480	.2134	.2943	.3918	.4990	.4264	.3200	.1965
10	.0936	.1527	2280	.3231	.4331	.4769	.3610	.2361	.1500
5	.0841	.1515	.2389	.3465	.4687	.4068	.3040	.1620	.0450
3	.0838	.1568	.2511	.3763	.4660	3600	.2460	.1160	—
2	.0850	.1564	.2653	.4125	.4436	.3370	.2200	—	—
1	.0694	.1509	.2823	.4645	.3996	.2590	.1280	—	—
0.5	.0695	.1602	.3308	.4700	.3723	.2139	—	—	—
0.05	.0176	.2922	.4600	.3668	.2620	—	—	—	—

TABLE VI

Corrected Power factor—temperature data at different frequencies

Frequency in Kc/s	Power factor, tan δ (corrected for D.C. conductivity) at the temperature of (°C)								
	10°	20°	30°	40°	50°	60°	70°	80°	90°
500	.0304	.0405	.0499	.0564	.0666	.0802	.0863	.0910	.0778
100	.0302	.0386	.0483	.0603	.0716	.0820	.0871	.0727	.0550
50	.0307	.0388	.0485	0633	.0752	.0841	.0828	.0658	.0473
25	.0287	.0389	.0515	.0654	.0796	.0890	.0703	.0510	.0413
10	.0260	.0391	.0535	.0691	.0833	.0800	.0575	.0370	.0235
5	.0230	.0383	.0548	.0719	.0862	.0664	.0476	.0251	.007
3	.0226	.0390	.0563	.0752	.0830	.0575	.0379	.0178	—
2	.0236	.0380	.0583	.0806	.0757	.0523	.0333	—	—
1	.0181	.0361	.0601	.0870	.0060	.0387	.0190	—	—
0.5	.0176	.0370	.0670	.0820	.0565	.0310	.0200	—	—
0.05	.0042	.0601	.0800	.0560	.0380	—	—	—	—

(b) *Hard Lac Resin*

TABLE VII

Dielectric constant—temperature data at different frequencies

Frequency in Kc/s	Dielectric constant ε′ at the temperature of (°C)						
	30°	40	50°	60°	70°	80°	90°
500	3·54	3·64	3·93	4·22	4·52	5·00	5·42
100	3·65	3·74	4·03	4·36	4·74	5·32	5·97
50	3·69	3·77	4·08	4·42	4·80	5·55	6·18
25	3·72	3·80	4·10	4 44	5·00	5·76	6·38
10	3·76	3·82	4·15	4·54	5·12	5·84	6·60
5	3·77	3·85	4·18	4·60	5·29	6·01	6·90
3	3·80	3·87	4·23	4·66	5·41	6·21	7·10
2	3·82	3·90	4·30	4·78	5·53	6·35	7·24
1	3·85	3·96	4·33	4·95	5·76	6·60	7·37
.05	3·90	4·09	4·54	5·25	5·37	7·57	8.13

TABLE VIII

Measured power factor data at different temperatures and frequencies

Frequency in Kc/s	Power factor (uncorrected) at the temperature of (°C)						
	30°	40°	50°	60°	70°	80°	90°
500	.0327	.0279	.0307	.0350	.0418	0554	.0664
100	.0237	.0194	.0221	.0289	.0448	.0611	.0756
50	.0187	.0157	.0188	.0253	0446	.0717	.0773
25	.0149	.0141	.0188	.0265	.0462	.0907	.0806
10	.0126	.0128	.0153	.0295	.0569	0783	0831
5	.0105	.0107	.0135	.0278	.0612	.0818	.0786
3	.0084	.0064	.0118	0234	.0659	.0868	.0713
2	.0085	.0036	.0072	.0211	.0676	.0900	.0672
1	.0072	.0012	.0023	.0183	.0694	.0823	.0562
0.05	.0051	.0010	.0032	.0285	.0818	.0612	.0200

TABLE IX

Dielectric loss—temperature data at different frequencies

Frequency in Kc/s	Dielectric loss ε'' (corrected) at the temperature of (°C)						
	30°	40°	50°	60°	70°	80°	90°
500	0.1156	0.1015	0.1206	0.1479	0.1888	0.2726	0.3582
100	0.0867	0.0724	0.0888	0 1262	0.2125	0.3253	0.4482
50	0.0688	0.0591	0.0769	0.1119	0.2145	0.3972	0.4753
25	0.0553	0 0535	0 0773	0.1179	0.2309	0.5170	0.5081
10	0.0472	0.0488	0.0635	0.1338	0.2914	0.4573	0.5484
5	0.0394	0.0414	0.0565	0.1277	0.3240	0.5032	0.5347
3	0.0321	0.0249	0.0498	0.1091	0.3565	0.5463	0.5012
2	0.0325	0.0141	0.0309	0.1009	0.3736	0.5556	0.4753
1	0.0275	0 0048	0.0097	0.1908	0.3995	0.5400	0.4103
.05	0.0203	0.0041	0.0141	0.1502	0.5243	0.4512	0.1532

(*c*) *Lac-Wax*

TABLE X

Dielectric constant—temperature data at different frequencies

Frequency in Kc/s	Dielectric constant ε' at the temperature of (°C)									
	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
500	2.60	2.61	2.60	2.61	2.62	2.63	2.68	2.69	2.67	2.63
100	2.62	2.62	2.62	2.64	2.65	2.66	2.70	2.70	2.67	2.63
10	2.69	2.68	2.69	2.68	2.59	2.69	2.76	2.72	2.68	2.63
1	2.77	2.78	2.77	2.75	2.76	2.76	2.79	2.74	2.68	2.63

TABLE XI

Measured power factor data at different temperatures and frequencies

Frequency in Kc/s	Power factor (uncorrected) at the temperature of (°C)									
	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
500	.0082	.0110	.0142	.0123	.0107	.0104	.0042	.0034	.0001	.0010
100	.0100	.0098	.0118	.0137	.0145	.0106	.0076	.0068	.0004	.0008
10	.0120	.0110	.0135	.0127	.0085	.0068	.0078	.0034	.0016	.0035
1	.0013	.0012	0013	.0009	.0009	.0003	—	—	—	—

DISCUSSION

We shall analyse the dielectric data collected for the three constituents of lac and discuss their implications separately. In a previous paper (Bhattacharya, 1944) the dielectric behaviour of whole lac has been fully discussed and in this paper referenee to that earlier communication will be frequently made in order to avoid repetition of the conclusions drawn previously. Of

the three constituents the most complete study could be made of the soft lac resin owing to the comparative ease with which this resin could be handled at high temperatures without the apprehension of its being heat-hardened unlike whole lac or hard lac. Shellac wax was even better in this respect but it would be seen that it behaves almost like a non-polar wax and so a complete analysis of its dielectric data is not necessary. Practical difficulties, as stated in the previous section, stood in the way of recording dielectric data of hard lac resin at temperatures higher than 90°C.

Soft lac resin.—The power factor—temperature curves have been shown in figures 1 and 2. Figure 1 shows the variation of power factor of soft lac with temperature as measured, *i.e.*, without any correction for the d.c. conductivity of the material whilst figure 2 shows the pure a.c. power factor—*i.e.*, after correcting for the d.c. conductivity—plotted against temperature. The nature of these curves is similar to those obtained for whole lac and in general for polar liquids. Each curve rises gradually to its maximum height and then falls again. The maximum point is indicated by a temperature which is characteristic of a frequency. Unlike curves for whole lac however the maximum value of power factor practically remains the same for all frequencies and is about 0.085—0.90. For whole lac the maximum value was 0·105 at 50 cycles/second and with increasing frequency it gradually fell to 0.0805 at 100 Kc/s. At 50 c/s the maximum power factor of soft resin takes place at so low a temperature as 27.5°C, whereas at 500 Kc/s this occurs at 79°C. The value of power factor at 22°C for practically all frequencies above 500 c/s is about 0·04 and at both higher or lower temperatures it varies with frequency.

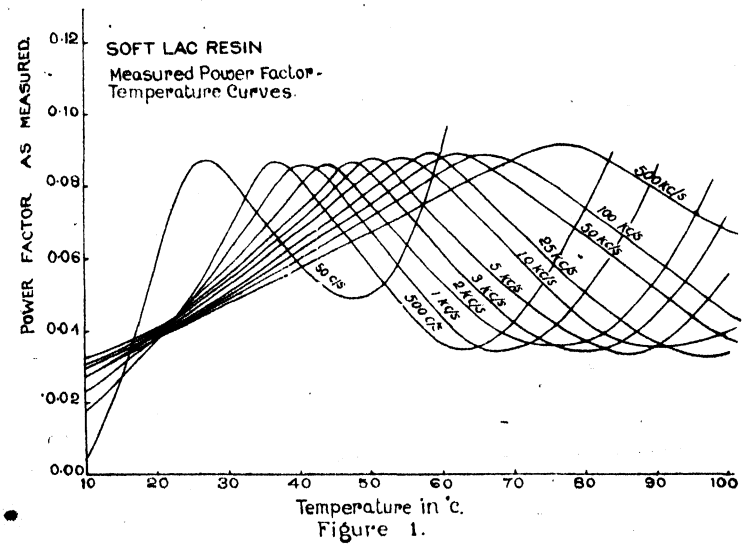


Figure 1.

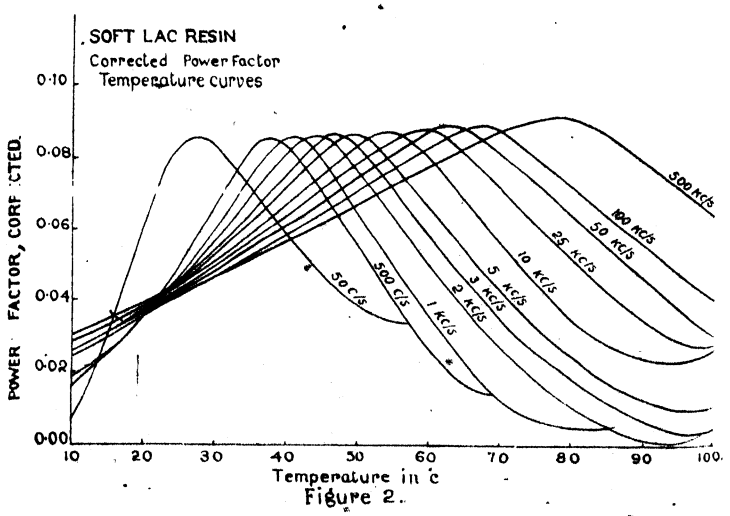
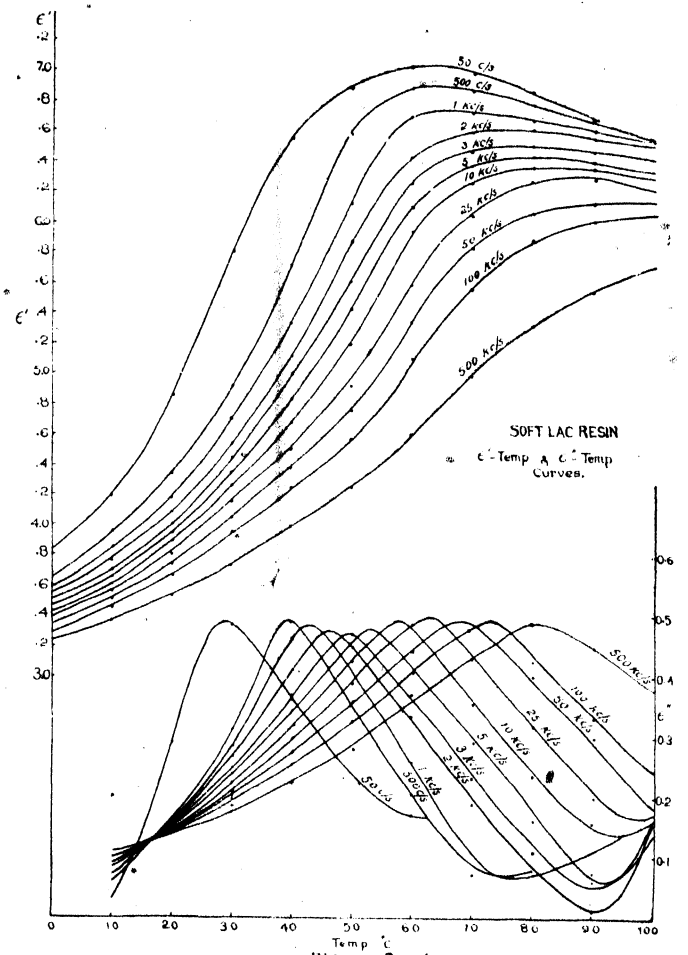


Figure 2.

The dielectric constant—temperature curves and the dielectric loss—temperature curves have been shown in figures 3 and 4. They are typical polar resin curves. Each curve in figure 3 is characterised by a sudden rise in dielectric constant and afterwards by a tendency

towards a flat maximum followed by a slow decrease in the flat maximum value. For whole lac the drooping portion of such curves could not be obtained since it occured at higher temperatures than 110°C and there was the apprehension of considerable heat hardening in the resin at such temperatures. For soft lac, however, there was no such difficulty and a complete curve could be obtained. The maximum value of dielectric constant for any frequency is lower for soft resin than for whole lac as may be seen from the curves. Thus ϵ_m' for soft lac at 50 c/s is 7.0, for 500 c/s it is 6.9 and for 1, 3, 5, 10, 50 and 100 Kc/s the respective values are 6.75, 6.50, 6.44, 6.38, 6.15 and 6.10, whereas for whole lac the respective values are higher even at 110°C.



Figures 3 & 4

The dielectric loss curves are also similar to those of whole lac. The maximum loss ϵ_m'', however, is less and is less than 0.5 for all frequencies. The general nature of these curves is also similar to those of lac except that no definite decreasing tendency in the ϵ_m'' value with rising frequency can be noticed.

Now as in the case of lac we can just get an idea of the relaxation time of the soft lac molecule from the relation

$$\epsilon_m'' = \frac{\epsilon_0' - \epsilon'_\infty}{2}$$

where ϵ_m'' = the maximum value of dielectric loss,

ϵ_0' = the static dielectric constant,

and ϵ_∞' = the low temperature value of dielectric constant.

Adopting the estimated value 7.5 for ϵ_0' and 3.5 for ϵ_∞' at 60°C (from figure 5) we see that the maximum loss value should have been 2.0 according to the simple Debye theory, but actual ϵ_m'' obtained is only 0.5 which is only a quarter of the calculated value. Hence, although the soft resin molecule has a comparatively lower molecular weight, a distributed range of relaxation times is suggested for this smaller molecule too. It has been already mentioned

how the effect of a distributed range of relaxation time in a molecule can be shown from theoretical grounds (Yager, 1936) to diminish the ϵ_m'' values and also to widen the dispersion band. In order to show the spread of the dispersion band in this case, figures 5 and 6 have been included. From figure 6 it may be seen that the band spreads over a very wide range, *viz.*, for at least 5 or 6 decades. From both these considerations, *viz.*, the diminished ϵ_m'' value as well as the widespread dispersion range, a distributed range of relaxation time of the soft resin molecule suggests itself. If ϵ''/ϵ_m'' values are plotted against f/f_m, which may be easily be computed from the ϵ''—log f graph, more bluntness or flatness of the curve than the Debye graph shows the effect of distributed relaxation time in the molecule. A comparative study of the degree of such an effect in different molecules may be made by the plot of such curves in a single graph, where more blunt curves will indicate greater effect of distributed relaxation time and the coincidence with the Debye curve will naturally show absence of distribution, *i.e.*, a single relaxation time. Fig. 7 shows such a graph for soft lac resin and the existence of a distributed range of relaxation time in the molecule may be seen from the bluntness of the curve. A comparison with the whole lac curve can also be made from this graph for which curve (B) has been included This is for Kusmi lac resin taken from the previous paper (Bhattacharya, 1944). It is observed that the bluntness of the soft lac curve (curve A) is slightly less than the Kusmi whole lac curve (curve B). This is just what may be expected since the soft lac molecule being smaller in size than the whole lac molecule should follow more closely the ideal Debye curve meant only for small polar molecule with a single relaxation time.

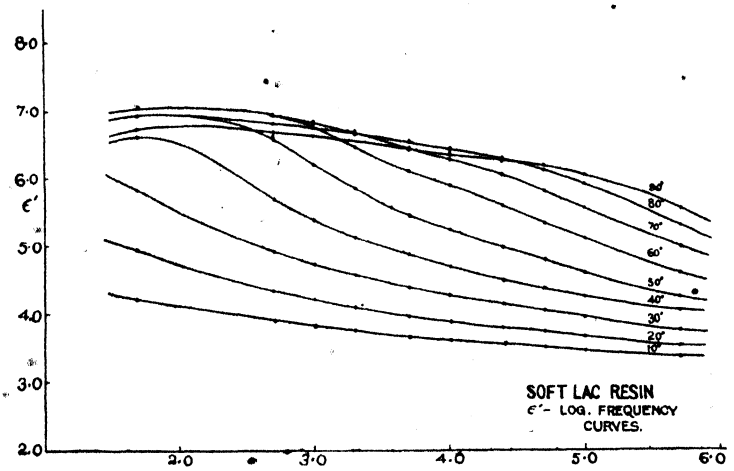


Figure 5.

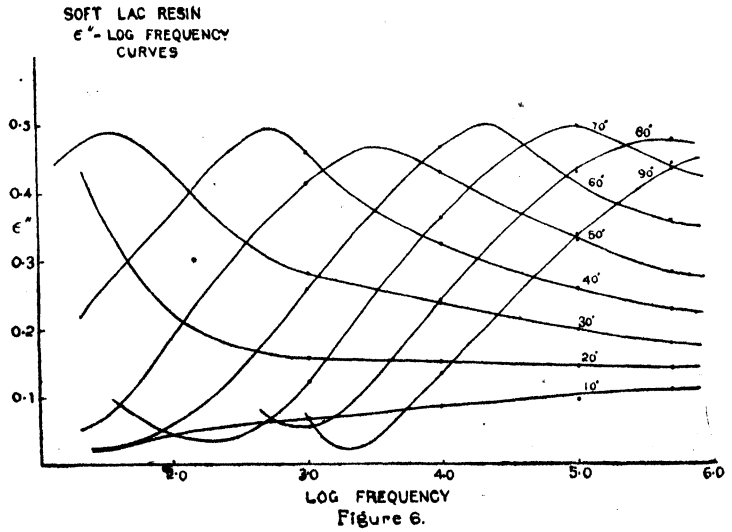


Figure 6.

A method of finding out the distribution coefficient of relaxation times of a polar molecule has very recently been given by Fuoss and Kirkwood (1941). They observe that for polar resins the loss factor ϵ'' can be represented by the approximate equation

$$\epsilon = A \operatorname{sech} \alpha x$$

where A is a constant, characteristic of the resin and derivable from dielectric constant data, α is the parameter which measures the width of the distribution and x is the natural logarithm of the ratio of the frequency at maximum absorption to the frequency at which ϵ'' is measured. They have also given a method whereby α, the distribution parameter of relaxation times of a polar system can be calculated from the observed loss factor—frequency curves. By following their method of calculation a value of 0.40 was obtained for α, the distribution parameter of soft lac. It may be remembered that α gave a value of 0.35 for Kusmi lac, and that distribution coefficient of relaxation times may be compared favourably with the distribution parameter of a resin system containing 80% polyvinyl chloride and 20% diphenyl (Fuoss and Kirkwood, *loc. cit.*). Soft lac resin has a still higher value of distribution parameter and in order to get an idea of this distribution by comparison with a polyvinyl chloride—diphenyl system we can only observe that a much higher percentage of the plasticiser will be required to yield a similar resin.

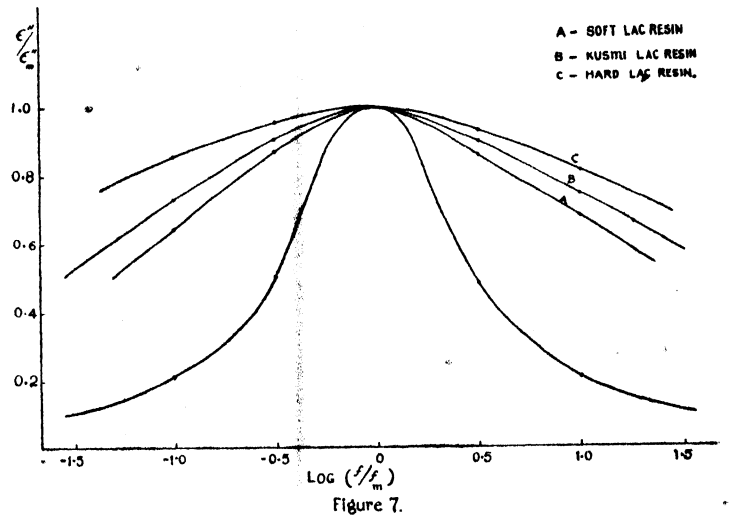


Figure 7.

Now in order to get an idea of the dimensions of the rotating unit, which contributes to the dielectric loss, we can use the relation

$$\tau = \frac{4\pi\eta a^3}{kT}$$

where τ = relaxation time of the rotator,

η = coefficient of viscosity,

a = radius of the rotator,

k = Boltzman constant,

and T = Temperature on Absolute scale.

τ can be calulated by means of the equation

$$\omega\tau = \frac{\epsilon_\infty' + 2}{\epsilon_0 + 2}$$

at the point where maximum dielectric loss takes place for any frequency in the loss factor—temperature ($\epsilon'' - t$) graph ϵ' and ϵ_0' are the values of dielectric constant at infinite and

zero frequencies respectively *i.e.*, dielectric constant at very high frequencies or low temperatures and that at very low frequencies or the static value of the dielectric constant respectively. These values may be estimated from ϵ' – log f graph and can be used in the calculation of relaxation time τ.

But the viscosity of soft lac resin at different temperatures was not known. In order to collect viscosity data of soft lac, therefore, a set of Lee's modified Ostwald viscometer usually meant for measurement on tar (Lee, 1934) was employed. The results have been shown in Table VII, it may be observed that these data can be represented by the usual logarithmic formula $\log\eta = A + \frac{B}{T} = A + \frac{Q}{RT}$

TABLE XII

Viscosity—temperature data

Temperature t°C	Temperature T°K	$T/1 \times 10^3$	Viscosity in poise η	$\log \eta$
55°	328	3·049	25,200	4·40
60°	333	3·003	10,100	4·00
70°	343	2·915	2,000	3·30
80°	353	2·833	503	2·70
90°	363	2·755	134	2·13

The graphical representation has been shown by the top line of figure 8. It was not possible to carry out the measurement of viscosity at any temperature below 55°C, as the viscosity seemed to be too high to be measured even with Lee's viscometer of the largest capillary diameter (6 mm.). From this graph, however, viscosity at any temperature within the range of measurement can be obtained.

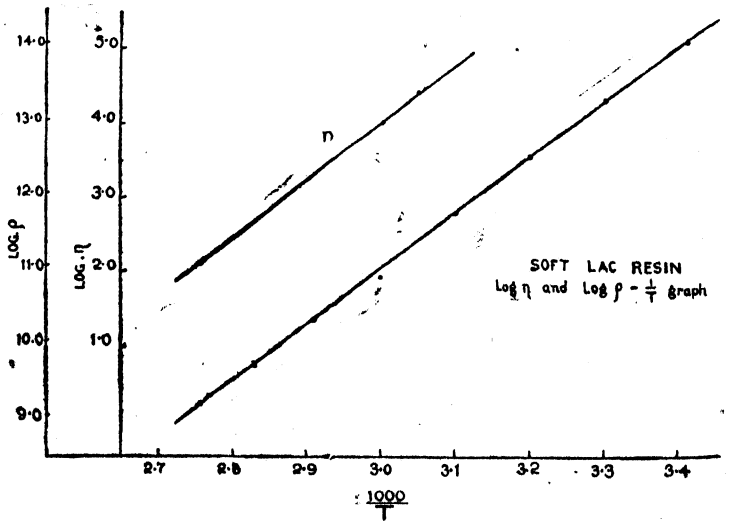


Figure 8.

Now the temperature of maximum loss at any frequency (Fig. 4) which falls within the above range of temperature may be taken and τ calculated from the relation

$$\omega\tau = \frac{\epsilon_\infty' + 2}{\epsilon_0 + 2}$$

The viscosity, corresponding to this maximum loss temperature, determined from the viscosity—temperature graph, may now be used in the equation

$$\tau = \frac{4\pi\eta a^3}{kT}$$

and thus the average radius of the rotating unit obtained. Table XIII shows the results of such calculations, from which it may be seen that, as in the case of whole lac, soft lac also yields practically the same value of radius for its rotator, *viz.*, about 1.50×10^{-8} cm. The conclusions arrived at previously have thus been strengthened by an independent set of measurements on soft lac and may, therefore, be repeated here. In the alternating current field the molecules of neither whole lac nor soft lac can rotate as a whole but the most probable polar group, *viz.*, the hydroxyl group takes part in the rotation. It is really very interesting that, on calculation from data obtained at different frequencies. practically the same value of radius has been obtained and that coincides with the radius of the most probably polar group in the molecule of either whole lac or soft lac. The only argument that can be placed against this calculation is the uncertainty regarding the inner friction coefficient of soft lac for which the macroscopic viscosity determined experimentally has been taken as equal. It has already been stated that the results of experiments with various polar liquids have shown that at least for liquids the macroscopic viscosity and the inner friction are the same, and from our present knowledge regarding the physico-chemical behaviour of thermoplastic resins we are inclined to include them in the category of liquids.

TABLE XIII

Calculated relaxation time and radius of the rotator

Loss max. temperature t°m	Relaxation time τ	Frequency f	Viscosity η	Radius of the rotator a
63°	4.00×10^{-6}	25 Kc/s	5×10^{3}	1.43×10^{-8} cm
69°	2.04×10^{-6}	50 Kc/s	2.4×10^{3}	1.47×10^{-8} cm
74°	1.02×10^{-6}	100 Kc/s	1.2×10^{3}	1.49×10^{-8} cm
83°	2.08×10^{-7}	500 Kc/s	2.63×10^{2}	1.45×10^{-8} cm

The relation $\tau = \frac{4\pi\eta a^3}{kT}$ is based upon Stoke's law which is generally applicable to liquids. But we can test from experimental data whether the inner frictional torque is proportional to macroscopic viscosity or not. To do this let us first of all assume that it is so. In that case we can write.

$$\tau = \xi / 2KT = C\,\eta/T$$

or,
$$T\tau = C\,\eta$$

or,
$$\log T\tau = C' + \log \eta$$

Substituting for $\log \tau$, the above relation can further be written as

$$\log T\tau = C'' + \frac{Q}{RT}, \quad [\text{since } \log \eta = A + \frac{Q}{RT}$$

where Q = molar activation energy and R = molar gas constant.

If the above assumption is true, a straight line graph is expected when log $T\tau$ is plotted against 1/T.

An actual plot for frequencies of 50 c/s, 1 Kc/s and 10 Kc/s shows that straight lines are obtained (Fig. 9). The relaxation time τ was calculated from the relation.

$$\tau = \frac{1}{\omega\epsilon''} \frac{\epsilon' + 2}{\epsilon_0' + 2} \left\{ \epsilon_m'' \pm \sqrt{\epsilon_m''^2 - \epsilon''^2} \right\}$$

Thus we see that the marcoscopic viscosity is at least proportional to inner friction, if not equal.

TABLE XIV

Log $T\tau$ and 1/T data

Frequency f	Temperature t°C	Temperature T°K	Relaxation time τ	$T\tau$	$1/T \times 10^3$	log $T\tau$
50 Kc/s	20°	293	67.0×10^{-4}	1.9630	3.413	0.2930
	30°	303	13.7×10^{-4}	0.4151	3.300	0.3819
	40°	313	63.7×10^{-5}	0.1993	3.195	0.7004
	50°	323	19.1×10^{-5}	0.0617	3.096	1.2098
1 Kc/s	20°	293	62.1×10^{-5}	0.1820	3.413	0.7400
	30°	303	31.4×10^{-5}	0.0951	3.300	1.0217
	40°	313	13.7×10^{-5}	0.0428	3.195	1.3678
	50°	323	47.8×10^{-6}	0.0154	3.096	1.8114
	60°	333	26.9×10^{-6}	0.0895	3.003	2.0478
10 Kc/s	20°	293	62.1×10^{-6}	0.0182	3 413	1.7400
	30°	303	41.2×10^{-6}	0.0125	3.300	1.9037
	40°	313	26.0×10^{-6}	0.0081	3.195	2.0895
	50°	323	17.0×10^{-6}	0.0055	3.096	2.2604
	60°	333	83.0×10^{-7}	0.0022	3.003	2.5585

Another checking of this may be made from the d.c. conductance data. The d.c. conductance of an insulating material is believed to be due to the mobility of its free ions. As the mobility is directly proportional to fluidity or inversely to viscosity at any temperature, an idea can be had as to how the inner friction varies with temperature from the d.c. conductance—temperature relation of the material. The bottom line of figure 8 shows that the logarithm of d.c. conductance Ko of soft lac gives a straight line plot with I/T throughout the whole range of investigation. And this straight line has

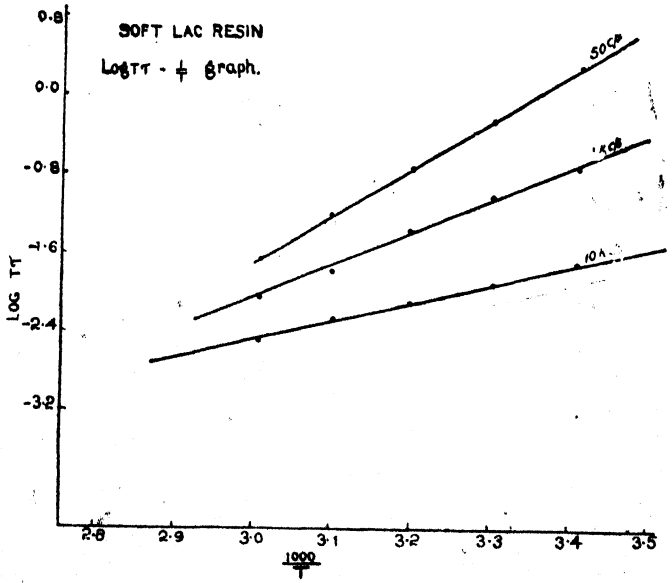
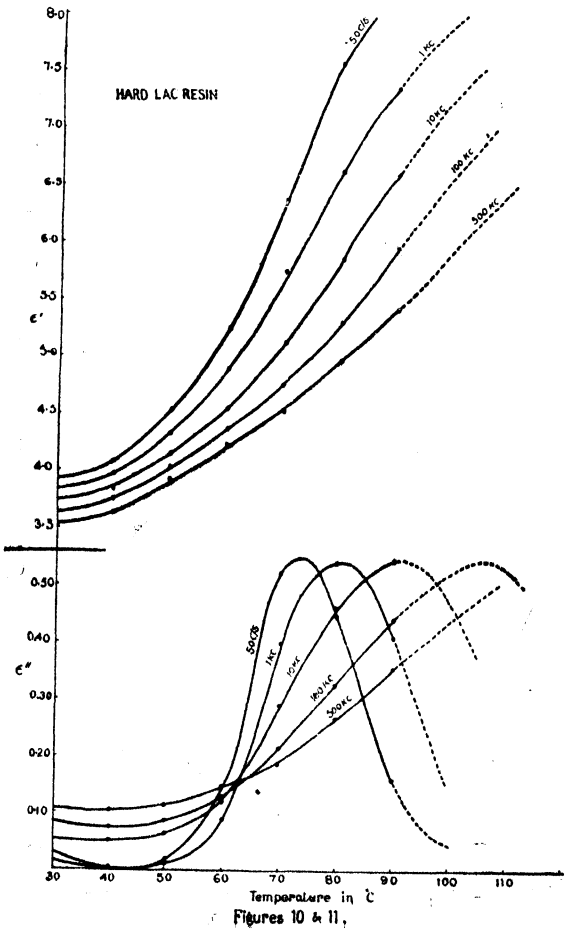


Figure 9.

practically the same slope with x-axis as the viscosity line, or in other words both of them have the same Q value. Thus we see from this angle of view too that the macroscopic viscosity and the inner friction vary exactly similarly with temperature.

Calculating frow the slope of these lines with 1/T axis, we find that the molar activation energy Q yields a value of 33.8 K-cal from d.c. conductivity data. Thus both these values are practically the same. Similarly the molar activation energy can be calculated from the log Tr-1/T graphs of figure 9. The value of Q will be different frequencies here, as is evident from the inclination of each line with the 1/T axis. The value of Q will be less and less with increasing frequency as is seen from the graph. In fact Q for 10 Kc/s is 8.0 K-calorie, for 1 Kc/s is 14.6 K-cal and for 50 c/s is 21.3 K-cal on calculation from the slope of these lines. Thus we see that the value of Q for still lower frequencies than 50 c/s will be greater than 21.3 K-cal and the value of about 34.0 K-cal obtained from the d.c. conductivity data is more or less in agreement with the value 33.0 K-cal obtained from the a.c. data by extrapolation to zero frequency.

If we compare these Q values with those of Kusmi lac calculated under similar conditions we find that the activation energy at 50 c/s is practically the same for both Kusmi lac and soft lac *viz.*, approximately 21.0 K-cal. But with the increase of frequency soft lac requires comparatively less energy than whole lac. Thus at 1 Kc/s soft lac requires about 15.0 K-cal whereas whole lac approximately 20.0 K-cal and at 10 Kc/s the value of Q for soft lac is only 8.0 K-cal whilst for whole lac it is 15.0 K-cal.



Figures 10 & 11.

The dielectric constant of soft lac even at 0°C is pretty high compared with the square of its refractive index at that temperature. The value of refractive index at 20°C is 1.4976 and computing from the temperature coefficient of refractive index (Bhattacharya, 1940) the value at 0°C may be estimated to be approximately 1.505. Hence we should expect that the dielectric constant of soft lac will be less and less at temperatures below zero till it approximates to the square of its refractive inflex at that temperature. This will happen when the dielectric constant will have the approximate value of 2.3, and assuming the linear variation at such low temperatures this may be expected to take place at—40°C or so.

Hard Lac Resin.—Measurements on hard lac discs could only be carried up to 80°C and with difficulty up to 90°C. Thereafter the discs began to get deformed due to softening. The results have, however, been shown in figures 10 and 11. For the sake of clearness in drawing curves at 50 c/s, 1 Kc/s, 10 Kc/s, 100 Kc/s and 500 Kc/s only have been drawn. They are just like Kusmi lac curves so far as could be judged from their nature and some of them have been extrapolated freely in order to study their nature at higher temperatures. The extrapolated part of each curve has been shown in broken line.

The first difference that may be noticed in these dielectric loss curves from the Kusmi lac ones is their similarity in the maximum height. The value of ϵ_m'', therefore, does not increase with decreasing frequency. Soft lac also showed more or less constant value of loss peak for all frequencies. If we take whole lac as a solid solution of pure lac in soft lac, the phenomenon of having increasing ϵ_m'' with decreasing frequency remains apparently unexplained. A further study of this abnormal behaviour of lac is being made and the result will be reported in another paper.

The loss peak of hard resin at 50 c/s takes place at 74°C whilst at 1 Kc/s, 10 Kc/s and 100 Kc/s the maximum loss probably takes place at 81°C, 91°C and 106°C respectively. The last two values are obtained by extrapolation and so may not be accurate. Comparing with soft lac and whole lac it appears that for any frequency the loss curve of hard lac takes up the extreme right position on the same temperature axis, that of whole lac the middle position and the soft lac curve the left position. The softening points of these resins are also in this order and if whole lac is looked upon as hard lac plasticised with soft lac each loss curve of hard lac will shift leftward, the amount of shift depending upon the soft resin content of lac. Such a behaviour has been observed by others (Davies, Miller and Busse, 1941 ; Fuoss, 1941) while experimenting with plasticised synthetic resins. The role of plasticiser is to shift any loss curve towards the left as a result probably of diminishing inner viscosity.

The ϵ'—frequency and ϵ''—frequency curves have been included in figures 12 and 13.

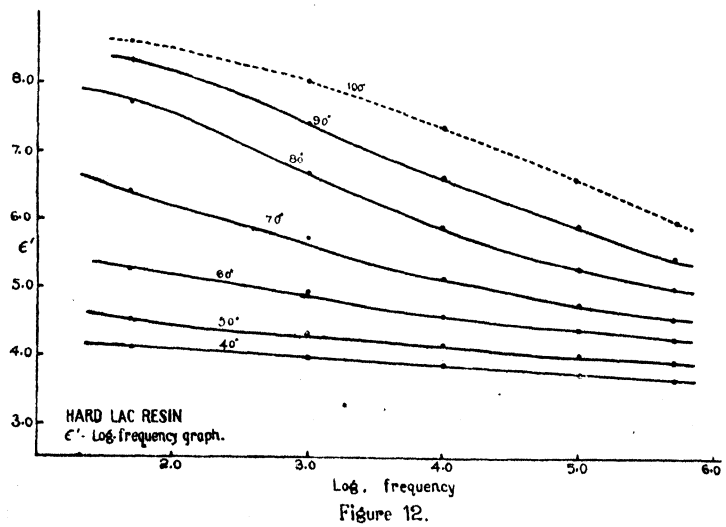


Figure 12.

From the loss curves it will appear that for hard lac the dispersion band is wider at any temperature than whole lac. The ϵ''/ϵ_m'' plot against f/f_m has been included in figure 7 along with soft lac. The 80°C data have been used for this purpose. Here also it may be seen that the curve for hard lac is more blunt than the Kusmi lac curve. Owing to the difficulty of measurement the viscosity data of hard lac could not be obtained and so the size of the hard lac rotating unit remains undetermined. But the distribution coefficient of relaxation times of the hard lac rotating unit could be determined according to the method of Fuoss

and Kirkwood and the value obtained for the distribution parameter was only 0.26. Thus we see that gives a value of 0.40, 0.35 and 0.26 for soft lac, whole lac and hard lac respectively showing thereby that of the three soft lac conforms most to the ideal Debye curve.

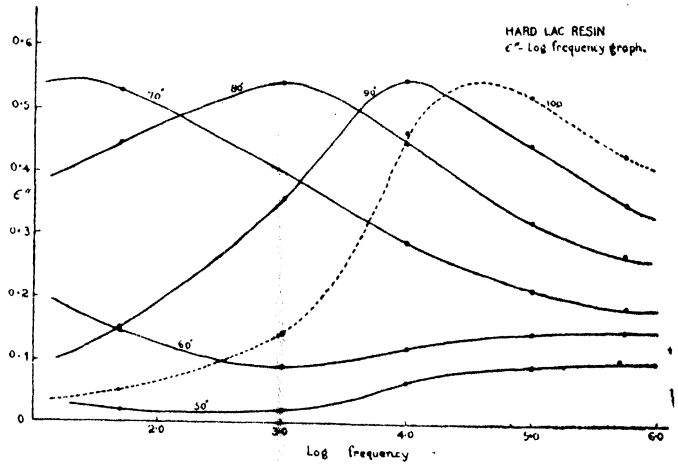
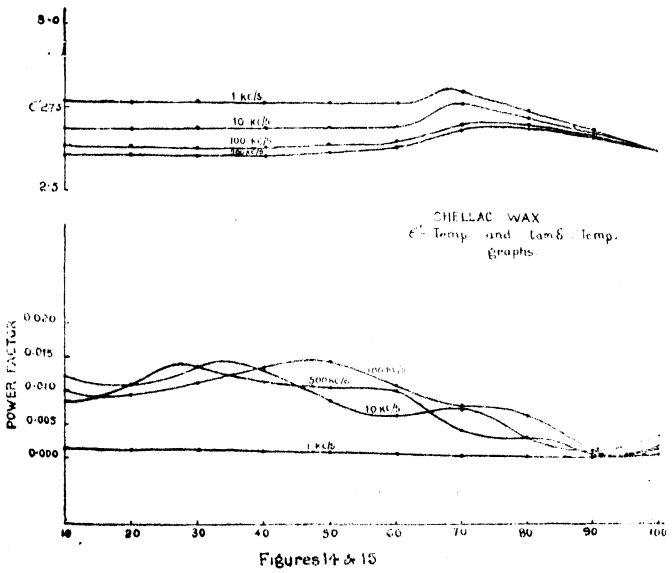


Figure 13.

We have seen that loss curves of Kusmi lac begin to rise abruptly between 35°C and 40°C ; for hard lac this happens after 50°C. For soft lac, however, such a point is difficult to obtain and if it exists at all this must be at a temperature below the experimental range, *i.e.*, below 10°C. The refractive index experiments also showed the existence of such a transition temperature for hard lac at 50°C or so (Bhattacharya, 1940). There it was observed that the temperature coefficient of refractive index of hard lac above 50°C was about three times that below it. But for soft lac no such temperature could be noticed and the temperature coefficient was uniform throughout the experimental range of temperature, *i.e.*, between 20°C and 90°C.

Lac-wax.—From the nature of dielectric constant-temperature graph (Fig. 14) it appears at first sight that lac-wax behaves almost as a non-polar substance. This lac-wax, it must be remembered, was purified from the commercial lac-wax, *i.e.*, it was only the alcohol soluble wax which is of course the main constituent comprising about 85% of the total. Tschirch and Schaefer (1926), investigated into the nature of this wax and they considered that it consisted of wax ester which on saponification gave an alcohol, probably $C_{25}H_{52}O$, and an acid $C_{26}H_{50}O_2$. On the evidence of crystal spacings, however, Chibnall and his co-workers (1934), are of the opinion that alcohol-soluble lac-wax is simply a mixture of primary alcohols of even number carbon atoms from C_{26} to C_{34}.



Figures 14 & 15

Alcohols are of course polar substances the molecules of which have an average moment of 1.68 Debye units but their dielectric constants decrease with the increase of carbon atoms

in the molecule. Thus dielectric constants of methyl and ethyl alcohol at 20°C are 31.2 and 25.8 whilst those of heptyl and octyl alcohols are 4.2 and 3.4 respectively. This may easily be explained if we consider that although the electric moment of the individual molecule of an alcohol remains practically the same the number of molecules per unit volume decreases with the lengthening of the carbon chain. Hence the dielectric constant is lowered. Baker and Smyth (1938), have recently studied the dielectric constant as well as the anomalous dispersion of cetyl alcohol, $C_{16}H_{33}OH$. They find that although the dielectric constant at 50 Kc/s near about 20°C is only 2.23 there is definite evidence of anomalous dispersion taking place just below the melting point of the alcohol, the dielectric constant at the melting point being about 4.30. We find from this that the variation of dielectric constant for the anomalous dispersion range is small and it may be expected that with a further increase of corbon chain this change of dielectric constant will be still smaller.

For lac-wax we find that a sudden discontinuity arises in the dielectric constant—temperature curve near about 60°C for practically all the frequencies used and above 80°C there is a tendency for all the curves to mix up. At 100°C or so the dielectric constant is practically independent of frequency. But at tempature below 60°C the dielectric constant is not independent of frequency but almost independent of temperature. The melting point of the wax was 83°C and the softening point 67°C, when determined by the mercury surface method (Rangaswami & Sen, 1942). From the temperature dependence of dielectric constant it appears, therefore, that the inner softening of the wax starts somewhat earlier than the temperature indicated by the softening point as determined by the mercury surface method. It should also be seen that even in the solid state of the wax there is some freedom of movement of the polar group—some form of dipole orientation—although general rotational freedom is not possible. This is clear from the frequency dependence of dielectric constant at low temperatures as well as from the inequality of these values from the square of the optical refractive index (about 2.2). The study of dielectric constant of many other solids has also indicated such a possibility. In the case of lac wax of course some explanation for the high value of dielectric constant just below the melting point of the wax is possible, *e.g.*, it being a physical mixture the presence of some components in the liquid phase just below the melting point of the wax is possible especially when a sharp melting point, as is generally obtained for pure organic compounds, is wanting here. But such an explanation is untenable at still lower temperatures, for all the components of this wax are primary alcohols containing no less than 26 carbon atoms and their individual melting points must be high. At ordinary temperatures all of them are expected to be solids and therefore the possibility of some amount of dipole orientation even at such a state should be entertained.

It is difficult to draw any useful conclusion from the power factor—temperature curves of lac-wax (figure 15). But we find that the power factor is extremely low at high temperatures when the wax is completely in the liquid phase. We thus see that all the molecules present in the wax can freely orient with the applied a.c. field after melting. This is possible because although their average molecular weight is about 450, being only primary alcohols they have simple structure. Their inner friction, therefore, is low and the resistance to orientation small. Hence the energy absorbed is small. The undulating nature of the curve at any frequency is probably the result of several peaks of which two are distinctly discernible.

It may now be noticed that lac-wax has no undesirable dielectric property which some people ascribe to it (Rangaswami and Sen, *loc. cit.*) noticing probably the widespread use of wax-

free shellac in some electrical industries. The use of de-waxed shellac has spread mainly for good adhesion and less water absorption of the varnish film and not for any undesirable dielectric property of lac wax. In fact the dielectric properties of lac wax are even better than those of either pure lac resin or soft lac regarding loss at slightly high temperatures. But its adhesion properties are poor since it is only a waxy material and not a resin and the water absorption of the de-waxed lac film has been found to be less than that of the whole lac film. Moreover the wax-free shellac film gives a more attractive appearance owing to its clearness and transparency although it suffers from some mechanical defects especially elasticity. Baking improves some of its mechanical properties and on comparing the properties of film produced from whole lac and wax-free lac one investigator (Rangaswami, 1933) is of the opinion that "a wax-free film or one with a low percentage of wax is preferable whenever baking is practicable as, for example, in the electrical industry." These are the reasons why wax-free lac is used in the electrical industry and not for any inferior dielectric property of lac wax.

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